



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

⑪ Publication number:

**O 013 139**

A1

⑫

## EUROPEAN PATENT APPLICATION

⑬ Application number: 79302979.4

⑮ Int. Cl.<sup>3</sup>: C 08 L 25/16

⑭ Date of filing: 20.12.79

⑯ Priority: 20.12.78 US 971178  
24.08.79 US 69481

⑰ Applicant: MOBIL OIL CORPORATION  
150 East 42nd Street  
New York New York 10017(US)

⑱ Date of publication of application:  
09.07.80 Bulletin 80/14

⑲ Inventor: Arbit, Harold Abraham  
35 North Sixth Avenue  
Highland Park, New Jersey 08904(US)

⑳ Designated Contracting States:  
BE DE FR GB IT NL

⑳ Representative: Cooper, John Anthony  
Mobil Court 3 Clements Inn-  
London WC2A 2EB(GB)

㉑ Blends of poly(p-methylstyrene) with polyolefins.

㉒ There is provided a blend of poly (p-methyl-styrene with small amounts of poly (C<sub>2</sub>-C<sub>4</sub>) olefin, olefin copolymer or styrene butadiene rubber. The blend can be formed into shaped articles, such as food containers, which can be cross-linked by irradiation at low doses. Such articles are resistant to microwave oven conditions.

EP 0 013 139 A1

BLENDs OF POLY(p-METHYLSTyRENE) WITH POLYOleFINS

This invention relates with blends of poly-(p-methylstyrene) with low molecular weight polyolefins and olefin copolymers which can be crosslinked by ionizing radiation at low dosage levels.

The present invention provides a blend of poly-(p-methylstyrene) with from 0.1 weight percent to 10 weight per cent low molecular weight poly (C<sub>2</sub>-C<sub>4</sub>) monoolefin, olefin copolymers or styrene butadiene rubber.

The monomer used in preparing the homopolymer or copolymers from which the blends of this invention are made is p-methylstyrene. It is within the contemplation of this invention to use mixtures of methylstyrene rich in p-methylstyrene. Such mixtures contain at least 95 weight percent, preferably 97-99 weight percent, p-methylstyrene and less than 0.1 weight percent o-methylstyrene with the balance being m-methylstyrene. A typical mixture contains, by weight, about 95 percent p-methylstyrene, about 5 percent m-methylstyrene, and about 0.5 percent o-methylstyrene. The mixtures are obtained by catalytic dehydrogenation of the mixtures of ethylmethyl benzene isomers described in U.S. Patent No. 4,086,287.

The polymers contemplated herein are p-methylstyrene or p-methylstyrene-rich isomer mixture homopolymer or their copolymers containing between about 10 and about 1 weight percent conjugated diene, such as butadiene and isoprene. The polymerization reaction is carried out by using methods and catalysts well known in the art for polymerizing styrene. The reaction can be carried out in solution, bulk, suspension, or emulsion.

In accordance with this invention, the material that is blended with the poly(p-methylstyrene) is a low molecular weight poly(C<sub>2</sub>-C<sub>4</sub>) olefin, olefin copolymer or styrene butadiene rubber. In general, molecular weights will be between about 2,000 and about 20,000 or higher. This material includes homopolymers of ethylene, propylene and butene-1 and copolymers thereof such as ethylene-propylene, butene-propylene or butene-ethylene. Also utilizable are copolymers of an olefin and an unsaturated monomer copolymerizable therewith such as ethylene-acrylate copolymers, e.g., ethylene acrylic acid and ethylene-ethyl acrylate or ethylene-vinyl acetate. Such polyolefins or olefin copolymers can be prepared by any of the processes well known in the art, usually under free radical conditions. A preferred material is low molecular weight polyethylene, which is described in U.S. Patents, such as Nos. 2,402,137; 2,504,400; and 2,683,141. Low molecular weight polyolefins, particularly polyethylene, are available commercially.

Small amounts of low molecular weight polyolefins or copolymers are effective to induce crosslinking by radiation at low dosage level. Generally, between about 0.1 weight percent and about 10 weight percent, preferably between about 0.5 weight percent and about 5 weight percent, will be used. Blending can be effected in a variety of ways, such as in solution in aromatic solvents such as toluene from which sheets or films can be cast. The blend components can be mixed in a tumbling agitator and fed into an extruder to produce sheets, films, or foamed sheets, or they can be fed separately to an extruder for extruder blending.

The blends of this invention can be formed into sheets, films, or foamed sheets and thermoformed to produce shaped articles, such as food containers. After being irradiated, such shaped articles are heat resistant and are not affected by fatty foods under microwave oven conditions.

Ionizing radiation is inclusive of extremely short-wave length, high energetic, penetrating rays such as gamma rays, X-rays, and subatomic particles accelerated in cyclotrons, betatrons, synchrotrons, and linear accelerators. The effect of irradiating the shaped articles is to crosslink the poly (p-methylstyrene) blend. The irradiation dose can be between about 20 megarads and about 45 megarads, whereas poly(p-methylstyrene) requires between about 50 megarads and about 60 megarads. Similar blends using polystyrene are not crosslinked at low dosages.

EXAMPLE 1

Poly(p-methylstyrene) (PPMS), containing 3% meta isomer and 0.1% ortho isomer, was dissolved in toluene at a concentration of 25 weight percent. Then, one weight percent low molecular weight, finely divided polyethylene (particle size 12 microns average) based on solid weight was added and dissolved. The polyethylene had a molecular weight of about 5,000-6,000 and density of 0.99 g./cc. Films were cast onto a smooth surface coated with polyethylene terephthalate and drawn down and dried to obtain a dried film thickness of about 2 mils. Film samples were irradiated by electron beam at various megarad (Mrads) doses. For each dosage level, crosslinking was determined by measuring solubility of the irradiated films in toluene at room temperature overnight. Any insoluble gel thus formed was filtered and dried to constant weight at 115°C. For comparison,

films of polystyrene (PS) containing one weight percent of the polyethylene used above were irradiated and tested for gel content. Pertinent data are set forth in the following Table I.

TABLE I

Gel. Content, %

Dose, M Rads	1% Polyethylene in	
	PPMS	PS
0	0	0
2	0	0
12	1.3	0
22	58.9	0
42	90.4	0
44	96.5	0

From the data in Table I, it will be noted that at doses between about 20 and about 45 M Rads substantial crosslinking of the blend of PPMS and polyethylene took place as measured by gelation, whereas PS blends did not crosslink. With PPMS alone (unblended), doses in the order of 50-60 M Rads were required. Thus, using the blends of this invention considerable energy savings are effected.

EXAMPLE 2

The run of Example 1 was repeated, except that the polyethylene used was one having a molecular weight of about 18,000 and a density of 0.924 g./cc. Pertinent data for irradiation of 2 mil films of the 1% blend in PPMS are set forth in Table II.

TABLE II

Gel Content, %

Dose, M Rads	1% Polyethylene in	
	PPMS	PS
0	0	0
10-12	0	0
40-42	93.1	0

EXAMPLES 3 TO 7

A series of blends with PPMS was prepared according to the procedure of Example 1, each containing one weight percent of a different polyolefin or olefin copolymer and films were made therefrom. Each film was irradiated by electron beam at various M Rad dosage levels. As described in Example 1, the amount of crosslinking was determined at each dosage level. Pertinent data and results are set forth in Table III.

0013139

-6-

TABLE III

Example No.	<u>ADDITIVE</u>	% GEL AT RADIATION LEVELS, M RAD'S			
		<u>0</u>	<u>2</u>	<u>12</u>	<u>44</u>
3.	Ethylene Acrylic Acid, Copolymer	92	0	.19	9.2
4.	Ethylene Vinyl Acetate, Copolymer	92	0	.05	30.1
5.	Polypropylene	0	0	.31	25.2
6.	Styrene Butadiene Rubber*	0	0	3.1	6.5
7.	Ethylene Propylene Rubber $\cong 30$	0	3.3	4.2	47.3
					57.9

\* About 30% styrene

1. A blend of poly(p-methylstyrene) with from 0.1 weight percent to 10 weight percent low molecular weight poly (C<sub>2</sub>-C<sub>4</sub>) monoolefin, olefin copolymer or styrene butadiene rubber.

2. The blend of claim 1 which contains from 0.5 to 5 weight percent of the poly (C<sub>2</sub>-C<sub>4</sub>) monoolefin, olefin copolymer or styrene butadiene rubber.

3. The blend of claim 1 or 2, wherein the poly (C<sub>2</sub>-C<sub>4</sub>) monoolefin is polyethylene having a molecular weight of about 5,000-6,000.

4. The blend of claim 1 or 2, wherein the poly (C<sub>2</sub>-C<sub>4</sub>) monoolefin is polyethylene having a molecular weight of about 18,000.

5. The blend of claim 2 which contains from 0.5 to 5 weight percent of styrene butadiene rubber.

6. The blend of claim 2 wherein the poly-(C<sub>2</sub>-C<sub>4</sub>) olefin is polypropylene.

7. The blend of claim 2 wherein the olefin copolymer is ethylene propylene rubber.



European Patent  
Office

EUROPEAN SEARCH REPORT

0013139  
Application number

EP 79302979.4

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	X 3
	<p><u>DE - B - 1 208 486</u> (CHEM. WERKE HÜLS)</p> <p>+ Column 1, lines 37-52; column 2, lines 19-30 +</p> <p>--</p> <p><u>GB - A - 1 328 446</u> (BASF)</p> <p>+ Claims 1 and 4 +</p> <p>--</p> <p><u>US - A - 3 880 790</u> (MC LAREN)</p> <p>+ Claims; column 3, lines 50-52 +</p> <p>--</p> <p><u>US - A - 3 753 961</u> (ST. CYR)</p> <p>+ Claim 1; column 4, lines 15-35 +</p> <p>--</p> <p><u>US - A - 3 586 740</u> (SCHOTT)</p> <p>+ Abstract; column 2, lines 48 - 65 +</p> <p>-----</p>	1-7  1,4  1  1-7  1,2,5	C 08 L 25/16
			TECHNICAL FIELDS SEARCHED (Int. Cl.) X 3
			C 08 L
CATEGORY OF CITED DOCUMENTS			
X	<p>The present search report has been drawn up for all claims</p>		<ul style="list-style-type: none"> <li>X: particularly relevant</li> <li>A: technological background</li> <li>O: non-written disclosure</li> <li>P: intermediate document</li> <li>T: theory or principle underlying the invention</li> <li>E: conflicting application</li> <li>D: document cited in the application</li> <li>L: citation for other reasons</li> </ul>
			<ul style="list-style-type: none"> <li>S: member of the same patent family,</li> <li>corresponding document</li> </ul>
Place of search	Date of completion of the search	Examiner	
VIENNA	20-03-1980	DICHER	